



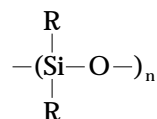
Silicone Chemistry Overview



Silicone Chemistry Overview

1. Introduction

By analogy with ketones, the name silicone was given in 1901 by Kipping to describe new compounds of the generic formula R_2SiO . These were rapidly identified as being polymeric and actually corresponding to polydialkylsiloxanes, with the formulation:

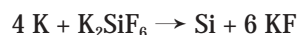


The name silicone was adopted by the industry and most of the time refers to polymers where $R = Me$ (polydimethylsiloxane). The methyls along the chain can be substituted by many other groups, e.g., phenyl, vinyl or trifluoropropyl. The simultaneous presence of “organic” groups attached to an “inorganic” backbone gives silicones a combination of unique properties and allows their use in fields as different as aerospace (low and high temperature flexibility), electronics (high electrical resistance), medical (excellent biocompatibility) and construction (resistance to weathering).

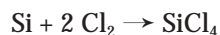
2. Historic

The principal steps in the development of silicone chemistry are^{1,2}:

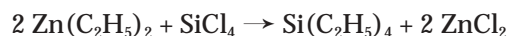
- The discovery of silicon by Berzelius in 1824 from the reduction of potassium fluorosilicate with potassium:



Reacting silicon with chlorine gave a volatile compound later identified as tetrachlorosilane, $SiCl_4$:



- The next step was made by Friedel and Craft with the synthesis of the first silicon organic compound in 1863, tetraethylsilane:

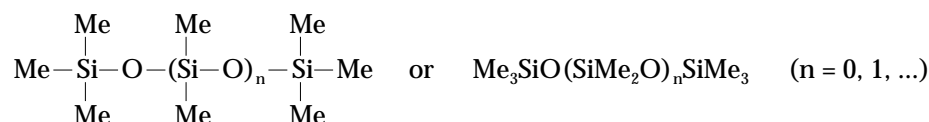


- In 1871, Ladenburg observed that, in the presence of a diluted acid, diethyldiethoxysilane, $(C_2H_5)_2Si(OC_2H_5)_2$, gave an oil that decomposed only at a “very high temperature.”
- Kipping laid the foundation of organosilicon chemistry with, among other things, the preparation of various silanes by means of Grignard reactions and the hydrolysis of chlorosilanes to yield “large molecules”; the polymeric nature of the silicones was confirmed by the work of Stock.

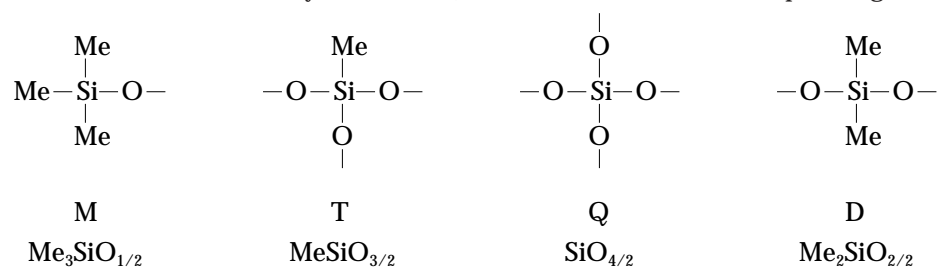
- In the 1940s, silicones became commercial materials after Hyde of Dow Corning demonstrated the thermal stability and high electrical resistance of silicone resins, and Rochow of General Electric found a direct method of preparing silicones from Si and MeCl.

3. Nomenclature

The most common silicones are the polydimethylsiloxanes trimethylsilyloxy terminated, with the following structure:



These are linear polymers and liquids, even for large values of n. The main chain unit, —(SiMe₂O)—, is often shortened by the letter D because, as the silicon atom is connected with two oxygen atoms, this unit is capable of expanding within the polymer in two directions. In a similar way, M, T and Q units can be defined corresponding to³:



The above polymer can also be described as MD_nM. It is possible to simplify the description of various structures like (Me₃SiO)₄Si or tetrakis(trimethylsilyloxy)silane, which becomes M₄Q (superscripts are sometimes used to indicate groups other than methyl).

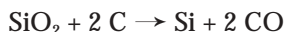
4. From Sand to Silicones

Silicones are obtained in a three-step synthesis:

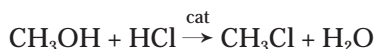
- chlorosilane synthesis
- chlorosilane hydrolysis
- polymerization and polycondensation

4.1 Chlorosilane Synthesis

Today, silicones are obtained commercially (± 500,000 t/y) from chlorosilanes prepared following the direct process of Rochow² and using Si metal obtained from the reduction of sand at high temperature:



and methylchloride obtained by condensation of methanol with hydrochloric acid:



The reaction giving chlorosilanes takes place in a fluidized bed of silicon metal powder in which a stream of methylchloride flows, usually at temperatures of 250 to 350 °C and at

pressures of 1 to 5 bars. A mixture of different silanes is obtained containing mainly the dimethyldichlorosilane, Me_2SiCl_2 ³:

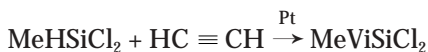
$x \text{ Si} + y \text{ CH}_3\text{Cl} \xrightarrow{\text{cat}}$		Yield (weight %)	Bp (°C)
	Me_2SiCl_2 [1]	> 50	70.0
	MeSiCl_3	10-30	66.4
	Me_3SiCl	< 10	57.9
	MeHSiCl_2	< 5	41.0
	other silanes	5	-

The reaction is exothermic and has a yield of 85 to 90%. A copper-based catalyst is used. The reaction mechanism is not completely understood. Chemisorption phenomena on active sites seem preferred to the radical-based mechanism originally proposed. The various silanes are separated by distillation. As the boiling points are close together, long distillation columns are always seen at silicone factories. The dimethyldichlorosilane [1] which is separated becomes the monomer for the preparation by hydrolysis of polydimethylsiloxanes (see further). Redistribution reactions can be used to convert the other silanes and increase the commercial yield of the production equipment⁴.

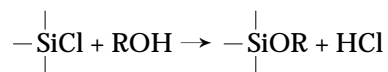
Ethyl- and phenylchlorosilanes can also be obtained through similar reactions to the direct process described above. Phenylchlorosilanes can also be prepared through a Grignard reaction³:



Other chlorosilanes are prepared from an existing silane, e.g., the methylvinyl-dichlorosilane is obtained by the addition of methyldichlorosilane on acetylene using a Pt complex as catalyst⁴:



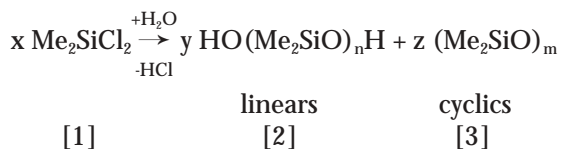
It is also possible to replace the chlorine groups by alcoholysis:



In this way, various silanes with different functionalities can be prepared, e.g., alkoxy and vinyl. These allow coupling reactions to take place between inorganic surfaces and polymers in composite manufacturing⁵.

4.2 Chlorosilane Hydrolysis

Polydimethylsiloxanes are obtained by the hydrolysis of the dimethyldichlorosilane in the presence of an excess of water according to³:



with $n = 20 - 50$ and $m = 3, 4, 5, \dots$ (mainly 4).

This heterogeneous and exothermic reaction yields a disilanol, $\text{Me}_2\text{Si}(\text{OH})_2$, which readily condenses, with HCl acting as a catalyst, to give a mixture of linear [2] or cyclic [3] oligomers by inter- or intramolecular condensation. This mixture separates from the

4.3 Polymerization and Polycondensation

aqueous acid phase, with the ratio between the two oligomers depending on the hydrolysis conditions (concentrations, pH, solvents). These oligomers are water-washed, neutralized and dried. The HCl is recycled and reacted with methanol to give the methylchloride used in the direct process described above.

The linear [2] and cyclic [3] oligomers obtained by hydrolysis of the dimethyldichlorosilane have too short a chain for most applications. They must be condensed (linears) or polymerized (cyclics) to give macromolecules of sufficient length⁶.

4.3.1 Cyclic polymerization

Opening and polymerizing cyclics, $(R_2SiO)_m$, to form long linear chains is catalyzed by many acid or base compounds⁴ and gives at equilibrium a mixture of cyclic oligomers plus a distribution of polymers. The proportion of cyclics will depend on the substituents along the chain, the temperature and the presence of a solvent. Polymer chain length will depend on the presence of substances capable of giving chain ends. For example, in the polymerization of $(Me_2SiO)_4$ with KOH, the average length of the polymer chains will depend on the KOH concentration:



[3]

A stable and -OH terminated polymer, $HO(Me_2SiO)_zH$, can be isolated after neutralizing and stripping the above mixture, under vacuum, of the remaining cyclics. In fact, a distribution of chains with different lengths is achieved.

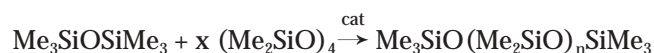
The reaction can also be made in the presence of $Me_3SiOSiMe_3$, which will act as a chain endblocker according to:



where $\sim\sim$ is the main chain.

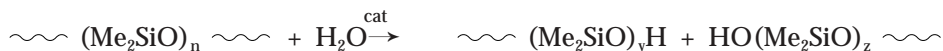
The Me_3SiOK formed will attack another chain to reduce the average molecular weight of the linear polymer formed.

The copolymerization of $(Me_2SiO)_4$ in the presence of $Me_3SiOSiMe_3$ with Me_4NOH as a catalyst displays a surprising viscosity change over time⁶. First, a peak or viscosity maximum is observed at the beginning of the reaction. With such a base catalyst, the presence of two oxygen atoms on each silicon in the cyclics makes them more susceptible to a nucleophilic attack by the catalyst than the silicon of the endblocker, which is substituted by one oxygen atom. The cyclics are polymerized first in very long, viscous chains that are subsequently reduced in length by the addition of terminal groups provided by the endblocker, which is slower to react. This reaction can be described as follows:



The ratio between D and M units will define the average molecular weight of the polymer formed.

Catalyst removal (or neutralization) is always an important step in silicone preparation. Most catalysts used to prepare silicones can also catalyze the depolymerization (attack along the chain), particularly in the presence of water traces at elevated temperatures:

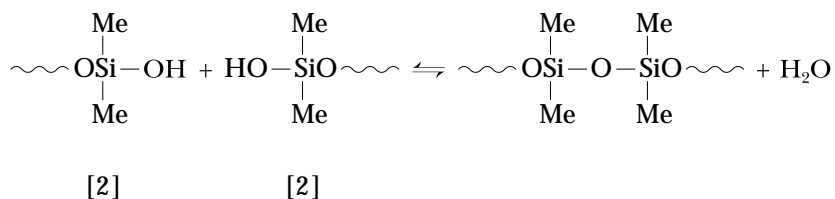


It is therefore essential to remove all remaining traces of the catalyst to benefit as much as possible from the silicone's thermal stability. Labile catalysts have been developed. These decompose or are volatilized above the optimum polymerization temperature and so can be eliminated by a brief overheating; in this way, catalyst neutralization or filtration can be avoided⁶.

The cyclic trimer, $(\text{Me}_2\text{SiO})_3$, is characterized by an internal ring tension and can be polymerized without re-equilibration of the resulting polymers. With this cyclic, polymers with narrow molecular weight distribution can be prepared, but also polymers carrying only one terminal reactive function (living polymerization). Starting from a mixture of different "tense" cyclics also allows the preparation of block or sequential polymers⁶.

4.3.2 Linear condensation

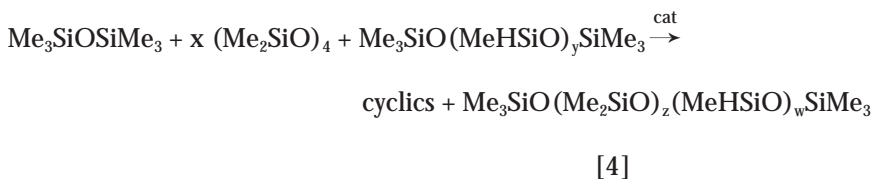
This reaction is catalyzed by many acids or bases^{4, 6}:



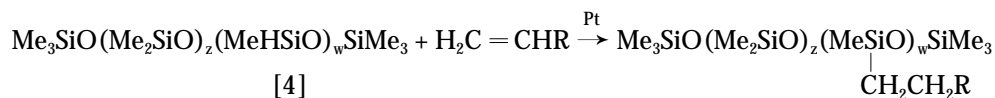
to give long chains by intermolecular condensation of terminals SiOH. A distribution of chain length is obtained and longer chains are favored when working under vacuum and/or at elevated temperatures to reduce the residual water concentration. Acid catalysts are more efficient when the organosilanol carries electron-donating groups, base catalysts when it carries electron-withdrawing groups. Some catalysts can induce a redistribution by attacking the polymer chain with the formation of cyclics. This is important when condensing a mixture of linear oligomers such as dimethyl- and methylphenyl-polysiloxanes. A sequential polymer will be obtained in the absence of redistribution, while a random polymer will result if a catalyst capable of opening the main chain is used.

4.3.3 Other polymers

Apart from the above polymers, reactive polymers can also be prepared. This can be achieved when re-equilibrating oligomers or existing polymers:

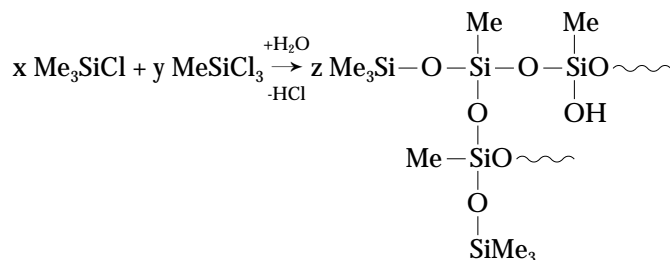


to obtain a polydimethyl-methylhydrogenosiloxane, $\text{MD}_z\text{D}_w^{\text{H}}\text{M}$. This polymer can be further functionalized using an addition reaction:



(R= alkyl, polyglycol,...)

The above polymers are all linear apart from the cyclics, but these are also made up of difunctional units, D. Apart from these, branched polymers or resins can be prepared if, during hydrolysis, a certain number of T or Q units are included, which will allow an expansion of the material, not in two but in three or four directions. This can be described if considering the hydrolysis of the methyltrichlorosilane in the presence of trimethylchlorosilane, which leads to:



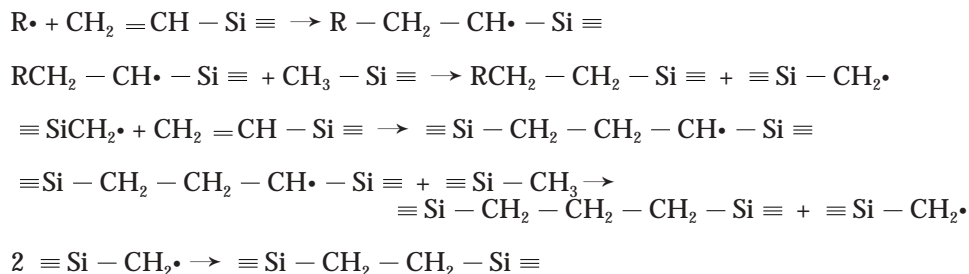
or $(\text{Me}_3\text{SiO}_{1/2})_x (\text{MeSiO}_{3/2})_y$ or M_xT_y . The formation, by hydrolysis, of three silanols on the MeSiCl_3 , yields a three-dimensional structure or resin, rather than a linear polymer. The average molecular weight depends upon the number of M units that come from the trimethylchlorosilane, which limits the growth of the resin molecule. Most of these resins are prepared in a solvent and usually contain some residual hydroxyl groups. These could subsequently be used to cross-link the resin and form a continuous network or varnish.

5. Silicone Cross-linking

5.1 Cross-linking with Radicals

The silicone polymers are easily transformed into a three-dimensional network and an elastomer via a cross-linking reaction that allows the formation of chemical bonds between adjacent chains. This is achieved according to one of the following reactions.

Efficient cross-linking with radicals is achieved only when some vinyl groups are present on the polymer chains. The following mechanism has been proposed for the cross-linking made by radicals generated from an organic peroxide⁴:

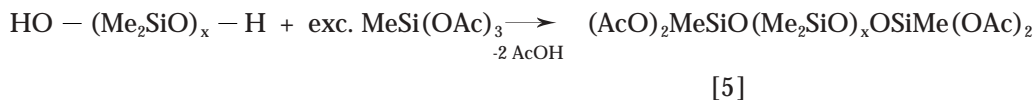


where \equiv represents 2 methyl groups and the rest of the polymer chain.

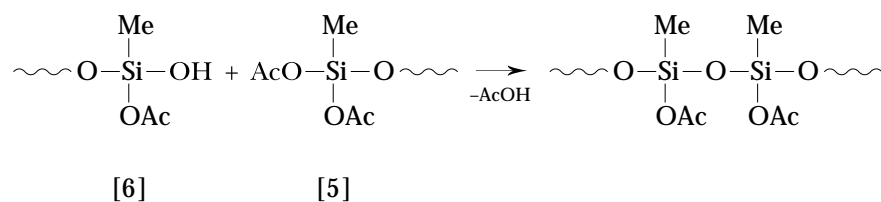
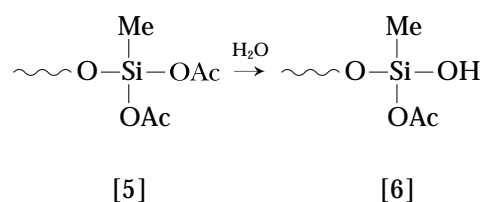
This reaction is used for high-consistency silicone rubbers (HCRs) like the ones used in extrusion or injection molding and which are cross-linked at elevated temperatures. The peroxide is added before use. During cure, some precautions are needed to avoid the formation of voids by the peroxide's volatile residues. Postcure may also be necessary to remove these volatiles, which can act as depolymerization catalysts at high temperatures.

5.2 Cross-linking by Condensation

This method is used in sealants such as the ones available in do-it-yourself shops. These products are ready-to-use and require no mixing. Cross-linking starts when the product is squeezed from the cartridge and comes into contact with moisture. They are formulated from a reactive polymer prepared from a hydroxy endblocked polydimethylsiloxane and a large excess of methyltriacetoxysilane:

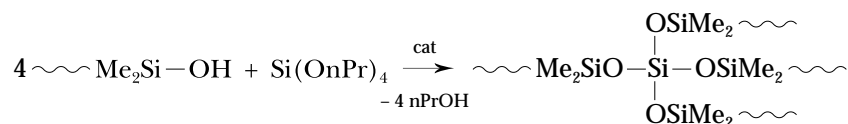


As a large excess of silane is used, the probability of two different chains reacting with the same silane molecule is remote and all the chains are endblocked with 2-OAc functions. The resulting product is still liquid and can be stored in sealed cartridges. Upon opening and contact with the moisture of the air, the acetoxy groups are hydrolyzed to give silanols that allow further condensation to occur:



In this way, two chains have been linked, and the reaction will proceed further from the remaining acetoxy groups. An organometallic tin catalyst is normally used. This cross-linking requires that moisture diffuses within the product and the cure will proceed from the outside surface toward the inside. These sealants are called one-part RTV (room temperature vulcanization) sealants, but they actually require moisture as a second component. Acetic acid is released as a by-product of the reaction and corrosion problems are possible on substrates such as concrete, with the formation of a water-soluble salt at the interface (and loss of adhesion at the first rain!). To overcome this, other systems have been developed, including one-part sealants releasing less corrosive or noncorrosive by-products, e.g., oxime using the oximosilane $\text{RSi}(\text{ON}=\text{CR}'_2)_3$ or alcohol using the alkoxy silane $\text{RSi}(\text{OR}')_3$ instead of the above acetoxy silane.

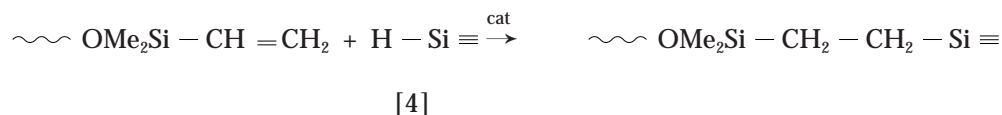
Condensation cure is also used in two-part systems where cross-linking starts upon mixing the two components, e.g., a hydroxy endblocked polymer and an alkoxy silane such as tetra n-propoxysilane⁶:



Here, no atmospheric moisture is needed. Usually an organotin salt is used as catalyst; however, to do so limits the stability of the resulting elastomer at high temperatures. Alcohol is released as a by-product of the cure, leading to a slight shrinkage upon cure. This precludes the fabrication of very precise objects (0.5 to 1 % linear shrinkage).

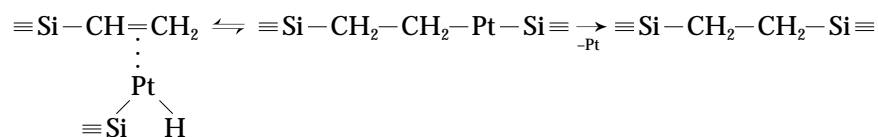
5.3 Cross-linking by Addition

The above shrinkage problem can be eliminated when using an addition reaction to achieve cross-linking. Here, cross-linking is achieved using vinyl endblocked polymers and reacting them with SiH groups carried by functional oligomers such as those described above [4]. A few polymers can be bonded to this functional oligomer [4], as follows⁴:



where \equiv represents the remaining valences of the Si in [4].

The addition occurs mainly on the terminal carbon and is catalyzed by Pt or Rh metal complexes, preferably organometallic compounds to enhance their compatibility. The following mechanism has been proposed (oxidative addition of the $\equiv \text{SiH}$ on the Pt, H transfer on the double bond, and reductive elimination of the product):



where to simplify, other Pt ligands and other Si substituents are omitted.

There is no by-product with this reaction. Molded pieces made with a product using this cure mechanism are very accurate (no shrinkage). However, handling these two-part products (polymer and Pt catalyst in one component, SiH oligomer in the other) requires some precautions. The Pt in the complex is easily bonded to electron-donating substances such as amine or organosulphur compounds to form stable complexes with these poisons, rendering the catalyst inactive (inhibition).

6. Properties of Silicones

Silicon, just under carbon in the periodic table, led to a belief in the existence of analogue compounds where silicon would replace carbon. Most of these analogue compounds do not exist or behave very differently. There are few similarities between Si-X bonds in silicones and C-X bonds^{3,4}:

Element (X)	Bond length (Å)		Ionic character (%)	
	Si-X	C-X	Si-X	C-X
Si	2.34	1.88	-	12
C	1.88	1.54	12	-
H	1.47	1.07	2	4
O	1.63	1.42	50	22

Between any given element and Si, bond lengths are longer than for C with this element. The lower Si electronegativity (1.8) vs. C (2.5) leads to a very polarized Si-O bond, highly ionic and with a large bond energy, 452 kJ/mole (108 kcal/mol). The Si-C bond has a bond energy of ± 318 kJ/mole (76 kcal/mol), slightly lower than a C-C bond, while the Si-Si bond is weak, 193 kJ/mole (46.4 kcal/mole). These values partially explain the

stability of silicones. The Si–O bond is highly resistant to homolytic scission. On the other hand, heterolytic scissions are easy, as demonstrated by the re-equilibration reactions occurring during polymerizations catalyzed by acids or bases (see above). Si atoms do not form stable double or triple bonds of the type sp^2 or sp with other elements, yet the proximity of the d orbitals allows $d\pi-p\pi$ retro-coordination. Because of this retro-coordination, trialkylsilanols are more acidic than the corresponding alcohols. Another example of the difference between analogues is the tetravalent diphenyldisilanol, $(C_6H_5)_2Si(OH)_2$, which is stable while its carbon equivalent, a gem-diol, will dehydrate. The Si–H bond is weakly polarized, but here in the direction of a hydride, and is more reactive than the C–H bond. Overall, there are few similarities between a silicone polymer and a hydrocarbon polymer.

Silicones display the unusual combination of an inorganic chain similar to silicates and often associated with high surface energy but with side methyl groups that are, on the contrary, very organic and often associated with low surface energy⁷. The Si–O bonds are strongly polarized and without protection should lead to strong intermolecular interactions⁴. Yet the methyl groups, only weakly interacting with each other, shield the main chain. This is made easier by the high flexibility of the siloxane chain. Rotation barriers are low and the siloxane chain can adopt many configurations. Rotation energy around a CH_2-CH_2 bond in polyethylene is 13.8 kJ/mol but only 3.3 kJ/mol around a Me_2Si-O bond, corresponding to a nearly free rotation. The siloxane chain adopts a configuration that can be idealized by saying that the chain exposes a maximum number of methyl groups to the outside, while in hydrocarbon polymers, the relative backbone rigidity does not allow a “selective” exposure of the most organic or hydrophobic methyl groups. Chain-to-chain interactions are low and the distance between adjacent chains is also higher in silicones. Despite a very polar chain, silicones can be compared to paraffin, with a low critical surface tension of wetting⁷.

The ease with which silicones adopt many configurations is confirmed by monolayer absorption studies on water. Two structures have been proposed, an open one in which the Si–O–Si bonds are oriented toward the aqueous phase, and a more compact one in which the chain adopts a helicoidal structure. The important point is the low energy difference between these two structures, again demonstrating the flexibility of the siloxane chain⁶.

The surface activity of silicones is displayed in many circumstances⁷:

- The polydimethylsiloxanes have a low surface tension (20.4 mN/m) and are capable of wetting most surfaces. With the methyl groups pointing to the outside, this gives very hydrophobic films and a surface with good release properties, particularly if the film is cured after application. Silicone surface tension is also in the most promising range for bio-compatible elastomers (20 to 30 mN/m).
- Silicones have a critical surface tension of wetting (24 mN/m) higher than their own surface tension; this means that silicones are capable of wetting themselves, which promotes good film formation and good surface covering.
- Silicone organic copolymers can be prepared with surfactant properties, with the silicone as the hydrophobic part, e.g., in silicone glycol copolymers.

The low intermolecular interactions in silicones have other consequences⁷:

- Glass transition temperatures are very low, e.g., 146 K for a polydimethylsiloxane compared to 200 K for polyisobutylene, the analogue hydrocarbon.
- The presence of a high free volume compared to hydrocarbons explains the high solubility and high diffusion coefficient of gas into silicones. Silicones have a high permeability to oxygen, nitrogen or water vapor, even if in this case liquid water is not capable of wetting a silicone surface. As expected, silicone compressibility is also high.
- In silicone, the activation energy to the viscous movement is very low, and the viscosity of silicone is less dependent on temperature than are the viscosities of hydrocarbon polymers. Moreover, chain entanglements are involved at higher temperature and limit the viscosity reduction.⁴

The presence of groups other than methyl along the chain leads to a reduction of the polymer's thermal stability, but with this substitution, some of the above properties can be modified:

- A small percentage of phenyl groups along the chain alters it sufficiently to affect crystallization and allow the polymer to remain flexible at very low temperatures. The phenyl groups also increase the refractive index.
- Trifluoropropyl groups along the chain change the solubility parameter of the polymer from 7.5 to 9.5 cal^{1/2}·cm^{3/2}. These copolymers are used to prepare elastomers with little swelling in alkane or aromatic solvents.

Note: this article (here revised) was originally published in Chimie Nouvelle, vol. 8 (30), 847 (1990) by A. Colas from Dow Corning Corporation.

7. References

- ¹ FEARON, F.W.G., *High performance polymers*, edit. R. Seymour and G. Kirschenbaum, Elsevier, 1986.
- ² ROCHOW, E.G., *Silicon and silicones*, Springer-Verlag, 1987.
- ³ HARDMAN, B., *Silicones*, Encycl. Polym. Sci. Eng., vol. 15, **204**, 1989.
- ⁴ STARK, F.O., *et coll.*, *Silicones*, Comprehensive Organometallic Chemistry, vol. 2, **305**, Pergamon Press, 1982.
- ⁵ PLUEDDEMAN, E.P., *Silane coupling agents*, Plenum Press, NY, 1982.
- ⁶ NOLL, W., *Chemistry and technology of silicones*, Academic Press, 1968.
- ⁷ OWEN, M.J., *Chemtech*, 11, **288**, 1981.



The information and data contained herein are based on information we believe reliable. You should thoroughly test any application, and independently conclude satisfactory performance before use. Suggestions of uses should not be taken as inducements to infringe any particular patent.

©1997 Dow Corning Corporation.
All rights reserved.

Printed in USA AMPM0105/397 Form No. 51-960A-97

DOW CORNING

**Dow Corning Corporation
Midland, Michigan 48686-0994**